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(54) DISPERSION STABILIZER FOR SUSPENSION POLYMERIZATION OF VINYL
COMPOUND

(57)Abstract:

PURPOSE: To provide a dispersion stabilizer which shows excellent dispersion formation and can produce a vinyl chloride resin excellent in reduced discoloration, when vinyl chloride monomer only or a monomer mixture containing the same as a main component is subjected to suspension polymerization.

CONSTITUTION: This dispersion stabilizer for suspension polymerization comprises a polyvinyl alcohol resin bearing carbonyl groups and containing a salt or hydroxide of a di- or trivalent metal in its molecule, preferably having ≥ 0.18 ultraviolet absorbance at wavelengths, 215nm, 280nm and 320nm, when 0.1wt.% resin aqueous solution is used for measurement.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the distributed stabilizer of the PVA system resin for the suspension polymerizations of the optimal vinyl chloride for excelling in dispersibility and obtaining a vinyl chloride system polymer particle with little coloring in more detail, about the distributed stabilizer of the polyvinyl alcohol (it may abbreviate to PVA hereafter) system resin used at the time of the suspension polymerization of a vinyl system compound, especially the distributed stabilizer of the PVA system resin for the suspension polymerizations of a vinyl chloride.

[0002]

[Description of the Prior Art] Before, the approach of carrying out the suspension polymerization of the mixture of a vinyl chloride monomer or a vinyl chloride monomer, and the monomer that may be copolymerized as an approach of manufacturing vinyl chloride resin industrially is learned. And at the time of the polymerization, distributed stabilizers, such as PVA, a methyl cellulose, a vinyl acetate-maleic-anhydride copolymerization object, and gelatin, are used, and the distributed stabilizer of various kinds of PVA(s) is examined according to the physical-properties improvement of the bulk density of the vinyl chloride system polymer (resin) particle obtained especially, particle size distribution, porosity, plasticizer absorptivity, a residual monomer, etc. The PVA system distribution stabilizer which paid its attention to the vinylene radical which adjoined the carbonyl group of PVA intramolecular and this from a viewpoint of raising the surface activity ability of a PVA system distribution stabilizer, also in this PVA system distribution stabilizer is proposed.

[0003] For example ** 280mmicro by the ultraviolet absorption spectrum of a 0.2-% of the weight water solution It partial-saponification-PVA(s) (JP,51-45189,A). (nm) -- 320 [and] -- the absorbance of m micro (nm) -- respectively -- 0.2 and 0.05 or more -- 280 -- 320 to m micro (nm) -- the ratios of the absorbance of m micro (nm) are 0.30-1.00 -- The ratio of a weight average degree of polymerization and a number average degree of polymerization ** Or less by 3.0 280mmicro by the ultraviolet absorption spectrum of a 0.1-% of the weight water solution It PVA(s) (JP,61-108602,A). (nm) -- 320 [and] -- the absorbance of m micro (nm) -- respectively -- 0.30 or more and 0.15 or more -- 280 -- 320 to m micro (nm) -- the ratio of the absorbance of m micro (nm) is 0.30 or more -- The absorbance of 280mmicro (nm) according [whenever / saponification] to the ultraviolet absorption spectrum of a 0.1-% of the weight water solution at 75-85-mol % ** 0.1 or more PVA (JP,5-105702,A) 50 degrees C or more is proposed [the content of a carboxyl group] for the cloudy point of a 0.01-0.15-mol % and 0.1-% of the weight water solution.

[0004]

[Problem(s) to be Solved by the Invention] However, the partial saponification PVA of above ** Since the vinylene radical which heat-treats by adding the univalent metal salt like sodium acetate to the partial saponification PVA as salts, and adjoins a carbonyl group is made to generate as indicated by the official report at the detail, conjugated system -- a long wave -- a merit side -- elongation -- easy -- it becoming PVA and the manufactured cause of coloring of PVC (polyvinyl chloride), and with this

disclosure technique, although PVA of practicability of above ** by these people and ** is also high If the generation effectiveness of a vinylene radical is low and tends to raise the amount of generation of this vinylene radical by heat treatment, insolubilization of PVA will tend to take place at the time of this processing. The amount of generation of a vinylene radical is raised, it has the room of an improvement still more in that surface activity ability will be raised further, and a distributed stabilizer of PVA system resin effective in excelling in the surface activity ability at the time of a suspension polymerization especially, and obtaining the particle of a vinyl chloride system polymer with little coloring (resin) was desired.

[0005]

[Means for Solving the Problem] As a result of this invention person's inquiring wholeheartedly in view of this situation, it has a carbonyl group in intramolecular. And 2 - trivalent a metaled salt or a metaled hydroxide is contained. Each absorbance of imputed] in the structure of imputed] and 320nm[-CO-(CH=CH)3- especially at the structure of imputed] and 280nm[-CO-(CH=CH)2- to the structure of 215nm[-CO-CH=CH- by the ultraviolet absorption spectrum of a 0.1-% of the weight water solution 0.18 or more When the PVA system resin which is 0.4 or more preferably uses as a vinyl system compound, especially a distributed stabilizer for suspension polymerizations of a vinyl chloride, While the obtained vinyl chloride system polymer (resin) particle satisfied general physical properties, such as bulk density and porosity, it found out excelling especially in dispersibility and having properties, like there is little coloring, and resulted in completion of this invention. Hereafter, this invention is explained to a detail.

[0006] The PVA system resin of this invention does not have a carbonyl group in intramolecular, and especially the manufacture approach is not limited. Carry out the polymerization of a well-known polymerization method, for example, the vinyl acetate, and polyvinyl acetate is manufactured. Oxidize the PVA system resin obtained in the usual process which saponifies this with oxidizers, such as a hydrogen peroxide, or Carry out the polymerization of the vinyl acetate under coexistence of an approach, 1-methoxy-vinyl acetate, etc. which prepare carbonyl group content PVA system resin by the approach of arbitration, such as performing a polymerization to the bottom of coexistence of a chain transfer agent, and polyvinyl acetate is manufactured. Although the approach of saponifying after blowing air at the time of the polymerization of the approach of saponifying this and obtaining carbonyl group content PVA system resin, or vinyl acetate and obtaining polyvinyl acetate, and using as carbonyl group content PVA system resin etc. is mentioned Especially the method of obtaining the PVA system resin which performs a polymerization under coexistence of chain transfer agents, such as aldehydes and ketones, saponifies the above-mentioned vinyl acetate monomer further industrially, and contains a carbonyl group is advantageous. Hereafter, this approach is explained further in full detail.

[0007] Acetone, methyl-ethyl-ketone, and hexa non, as a chain transfer agent used for this approach, an acetaldehyde, propionaldehyde, a butyraldehyde, a benzaldehyde, etc. are mentioned to aldehydes, and a cyclohexanone etc. is mentioned to it as ketones. Although the addition of a chain transfer agent changes somewhat with degrees of polymerization of PVA made into the chain transfer constant and the object of the chain transfer agent to add etc., 0.5 - 3 % of the weight is usually preferably desirable [an addition] 0.1 to 5% of the weight to a vinyl acetate monomer. Moreover, early package preparation is sufficient as an approach to teach a chain transfer agent, and you may also teach it at the time of a polymerization reaction, and the molecular weight distribution of PVA can be controlled by teaching by the approach of arbitration.

[0008] In carrying out the polymerization of the ~~vinyl acetate~~, there is especially no limit, a well-known polymerization method is used for arbitration, but the solution polymerization which usually uses alcohol, such as a methanol, ethanol, or isopropyl alcohol, as a solvent is carried out. Of course, bulk polymerization, an emulsion polymerization, and a suspension polymerization are also possible. The means of arbitration, such as division preparation and package preparation, may be used for an approach to teach a vinyl acetate monomer in this solution polymerization. A polymerization reaction is performed using well-known radical polymerization catalyst, such as azobisisobutyronitril, acetyl peroxide, benzoyl peroxide, lauroyl peroxide, azobis dimethylvaleronitrile, and azobis methoxy

valeronitrile. Moreover, reaction temperature is chosen from the range of 40 degrees C - boiling point extent.

[0009] Vinyl acetate and the monomer in which a polymerization is possible, for example, an acrylic acid, if required at this time The alkyl ester of unsaturated carboxylic acid, such as a methacrylic acid, a crotonic acid, a maleic acid, and maleic-acid monoalkyl, or these partial saturation acid, Nitril or amides, such as acrylonitrile, a methacrylonitrile, acrylamide, and methacrylamide, Olefin sulfonic acids or these salts, such as an ethylene sulfonic acid, an allyl compound sulfonic acid, and a meta-allyl compound sulfonic acid, It is also possible to carry out copolymerization of vinyl ester other than vinyl acetate, saturation branched chain fatty acid vinyl, vinyl ether, a vinyl ketone, ethylene, an alpha olefin, halogenation vinyl, the halogenation vinylidene, etc.

[0010] The vinyl acetate polymer obtained above in saponification is dissolved in alcohol, it is carried out to the bottom of existence of an alkali catalyst or an acid catalyst, and a methanol, ethanol, a butanol, etc. are mentioned as this alcohol. The concentration of the polymer in alcohol is chosen from 20 - 50% of the weight of the range. As an alkali catalyst, the alkali catalyst like the hydroxide of alkali metal, such as a sodium hydroxide, a potassium hydroxide, sodium methylate, sodium ethylate, and a potassium methylate, or an alcoholate can be used, and organic acids, such as inorganic-acid water solutions, such as a hydrochloric acid and a sulfuric acid, and p-toluenesulfonic acid, can be used as an acid catalyst. The amount of this catalyst used needs to make it the 1 - 100 millimol equivalent to vinyl acetate. In this case, especially a limit does not have saponification temperature, but it is usually desirable to choose out of the range of 20-50 degrees C preferably 10-70 degrees C. A reaction is usually performed over 2 - 3 hours.

[0011] Although the PVA system resin obtained in this way contains a carbonyl group in the intramolecular, more than 0.05 mol % is more than 0.1 mol % desirable still more preferably, and the content becomes [this content] inadequate [less than / 0.05 mol % / the amount of generation of a vinylene radical] and is not desirable. Moreover, 65-98-mol % is 67-90-mol % desirable still more preferably, and if whenever [this saponification] becomes poor [moisture powder] less than [65 mol %] and exceeds 98-mol % conversely, it is [surface activity ability falls, and the dispersibility of vinyl chloride monomer becomes poor, and] easy to generate a block at the time of a suspension polymerization and is not desirable [whenever / saponification / of this PVA system resin]. 50-4000 are 100-3000 desirable still more preferably, and the average degree of polymerization of this PVA system resin becomes [the vinylene radical weight of a PVA end is insufficient, and / surface activity ability] inadequate and is not desirable, if protective colloid nature becomes low too much, this average degree of polymerization lifting-comes to be easy of condensation by less than 50 at the time of a suspension polymerization and 4000 is exceeded conversely.

[0012] Furthermore, it is indispensable that the PVA system resin containing the carbonyl group like the above contains 2 - trivalent a metaled salt or a metaled hydroxide in this invention. Magnesium, calcium, zinc, aluminum, etc. can be illustrated as a metal 2- trivalent [this]. As the salt of these metals, or an example of a hydroxide Magnesium acetate 4 hydrate, calcium acetate, calcium propionate, Butanoic acid magnesium, a magnesium carbonate, a magnesium hydroxide, zinc acetate, an aluminum hydroxide, etc. are mentioned, and magnesium acetate 4 hydrate and calcium acetate are suitably used in that dissolve in water, a methanol, etc. and it is easy to deal with it industrially especially. That what is necessary is just to contain these compounds in the above-mentioned PVA system resin Although especially the addition approach is not limited but you may add directly to the slurry after the paste and saponification before saponifying the above-mentioned compound etc. The approach of making dissolve in alcohol, such as a methanol, ethanol, and propanol, or water preferably, having the shape of a solution of about 3 - 15% of the weight of concentration, adding to the PVA slurry after saponification, and making it distribute to PVA system resin is desirable. Moreover, as a content of this compound in PVA system resin, if it is 40-200micromol/g desirable still more preferably [mol //g / 30-300micro], and this content runs short of the amounts of generation of a vinylene radical and exceeds 300micromol/g conversely under by 30micromol/g to PVA, coloring or decomposition of PVA system resin become intense and are not desirable.

[0013] In this invention, although characterized by making 2 - trivalent a metaled salt or a metaled hydroxide contain like the above, it is also possible to use together univalent metallic compounds other than these compounds (for example, sodium acetate etc.) in the range (for it to be 1 or less % of the weight to 2 - trivalent a metaled salt or a metaled hydroxide) which does not check the effectiveness of this invention. Although it is desirable from the point of the introductory effectiveness of a vinylene radical to make the PVA system resin which contained the carbonyl group beforehand like the above contain 2 - trivalent an above-mentioned metaled salt or an above-mentioned metaled hydroxide in this invention, after making the PVA system resin which does not contain a carbonyl group contain 2 - trivalent an above-mentioned metaled salt or an above-mentioned metaled hydroxide, it is possible to also make a carbonyl group contain by heat treatment etc.

[0014] Although the PVA system resin obtained like the above has a carbonyl group in intramolecular and contains 2 - trivalent a metaled salt or a metaled hydroxide In the structure of 215nm[-CO-CH=CH- by the ultraviolet absorption spectrum of the 0.1-% of the weight water solution of this PVA system resin, especially Imputed], Each absorbance of imputed] in the structure of 280nm[-CO-(CH=CH)2- at the structure of imputed] and 320nm[-CO-(CH=CH)3- 0.18 or more Furthermore, the PVA system resin which is 0.4 or more can desire improvement in physical properties with the vinyl chloride polymer (resin) it is very useful as a distributed stabilizer for suspension polymerizations of a vinyl chloride, and new obtained. Hereafter, the adjustment approach of this PVA system resin is explained concretely.

[0015] Although not limited especially about this adjustment approach, the method of usually presenting specific heat treatment with PVA system resin is mentioned. 120-180 degrees C is desirable still more desirable, and the temperature conditions of this heat treatment are 140-155 degrees C. These temperature conditions at less than 120 degrees C If desired vinylene radical weight is not obtained but 180 degrees C is exceeded conversely, become [decomposition by heat treatment] intense and are not desirable. Moreover, it becomes the cause of coloring of PVA system resin, or the cause of insoluble content generation over water and is not desirable, if 0.5 - 5 hours is desirable still more desirable as time amount of heat treatment, the amount of generation of a vinylene radical runs short of this processing time in less than 0.5 hours in 1.5 - 5 hours and 5 hours is exceeded conversely. Moreover, heat-treating by melting extrusion etc. is also possible.

[0016] Moreover, it is under the ambient atmosphere of 3 - 12 capacity % that an oxygen density ^{oxygen density} performs the above-mentioned heat treatment under the oxygen ambient atmosphere below 20 capacity % desirable still more preferably. It is [a possibility of becoming the cause of insolubilization / **** / that coloring of PVA system resin becomes intense] and is not desirable when this oxygen density exceeds 20 capacity %. In this heat treatment, although the thing which made PVA obtained by the well-known approach contain the metal salt shown above can be used, in order to make the vinylene radical of amount sufficient in order to obtain good surface activity ability generate, as for the content of the carbonyl group of the PVA system resin before heat treatment, it is desirable that it is [0.03-2.5 mol] %. The PVA system resin obtained in this way In the structure of 215nm[-CO-CH=CH- by the ultraviolet absorption spectrum of a 0.1-% of the weight water solution, imputed], It is that by which each absorbance of imputed] was adjusted to the structure of 280nm[-CO-(CH=CH)2- by the structure of imputed] and 320nm[-CO-(CH=CH)3- 0.18 or more. Less than in 0.18, dispersion force declines and this absorbance is 0.4 or more desirable still more preferably.

[0017] Next, the suspension-polymerization approach of the vinyl system compound (vinyl chloride) using the PVA system resin of this invention as a distributed stabilizer is explained. In case a suspension polymerization is carried out, the PVA system resin of this invention is added as a distributed stabilizer to the indifferent water or a heating water medium, a vinylchloride monomer is distributed, and a polymerization is performed under existence of an oil solubility catalyst. This PVA system resin (distributed stabilizer) can be added by the shape of a solution with powder. Moreover, this PVA system resin can add as a water dispersion, when whenever [saponification] serves as a water dispersing element low (less than [67 mol %] extent). In the shape especially of a solution, when this PVA system resin is water solubility, it is a water solution, and it can be made to be able to dissolve in the mixed solvent of organic solvents, such as alcohol, a ketone, and ester, or these organic solvents, and water,

and, also in the case of a nonaqueous solution, can add as a solution. In a water dispersion, even if whenever [saponification] is low, when this PVA system resin has the self-dispersibility to water, it can add to a water dispersion as it is.

[0018] Package preparation of this distributed stabilizer may be carried out in early stages of a polymerization, or you may divide in the middle of a polymerization, and may also teach it. Moreover, as long as the catalyst used is an oil solubility catalyst, any are sufficient as it, for example, it is benzoyl peroxide, lauroyl peroxide, diisopropyl peroxy dicarbonate, alpha-alpha'-azobisisobutyronitril, and alpha-alpha' - Azobis -2, 4-dimethyl-valeronitrile, acetyl cyclohexyl sulfonyl peroxide, or such mixture are used. Polymerization temperature is chosen from the range of this contractor common knowledge as arbitration. Moreover, it is also possible to use together well-known stabilizers other than the PVA system resin of this invention, for example, a polymeric material. As a polymeric material, 0-95-mol % of PVA or, and its derivative is mentioned average degree of polymerization 100-4,000 and whenever [saponification]. As this derivative of PVA, an esterification object with the formal ghost of PVA, an acetal ghost, a butyral ghost, an urethane ghost, a sulfonic acid, a carboxylic acid, etc. is mentioned. Furthermore, the copolymer saponification object of vinyl ester, it, and a copolymerizable monomer is mentioned. As this monomer, ethylene, a propylene, an isobutylene, alpha-octene, Olefins, such as alpha-dodecen and alpha-octadecene, an acrylic acid, a methacrylic acid, partial saturation, such as a crotonic acid, a maleic acid, a maleic anhydride, and an itaconic acid, -- acids, its salt, monochrome, or dialkyl ester Nitril, such as acrylonitrile and a methacrylonitrile, acrylamide, Olefin sulfonic acids, such as amides, such as methacrylamide, an ethylene sulfonic acid, an allyl compound sulfonic acid, and a meta-allyl compound sulfone, or the salts of those, alkyl vinyl ether, a vinyl ketone, N-vinyl pyrrolidone, a vinyl chloride, a vinylidene chloride, etc. are mentioned. However, it is not necessarily limited to this.

[0019] As polymeric materials other than above PVA, moreover, methyl cellulose, ethyl cellulose, A hydroxymethyl cellulose, the hydroxypropyl methylcellulose, Hydroxy butyl methyl cellulose, hydroxyethyl cellulose, A carboxymethyl cellulose, aminomethyl hydroxypropylcellulose, Cellulosics, such as aminoethyl hydroxypropylcellulose Starch, tragacanth, pectin, GRU, an alginic acid, or its salt, Gelatin, a polyvinyl pyrrolidone, polyacrylic acid or its salt, Pori methacrylic acid, or its salt, Polyacrylamide, the poly meta acrylamide, vinyl acetate and a maleic acid, The salts or ester of a copolymer with partial saturation acids, such as a maleic anhydride, an acrylic acid, a methacrylic acid, an itaconic acid, a fumaric acid, and a crotonic acid, the copolymer of styrene and the above-mentioned partial saturation acid, the copolymer of vinyl ether and the above-mentioned partial saturation acid, and said copolymer is mentioned. It is also possible to use together various surfactants or an inorganic dispersant suitably as an assistant at the time of a polymerization, and it is also possible to use the PVA system resin of this invention as an assistant further.

[0020] Furthermore, not only homopolymerization of a vinyl chloride but copolymerization of this and a copolymerizable monomer is performed. As a copolymerizable monomer, halogenation vinylidene, vinyl ether, vinyl acetate, benzoic-acid vinyl, an acrylic acid, a methacrylic acid and its ester, a maleic acid or its anhydride, ethylene, a propylene, styrene, etc. are mentioned. Moreover, it is also arbitrary to add the modifier used suitably, a chain transfer agent, a gelation amelioration agent, an antistatic agent, PH regulator, etc. at the time of the polymerization of a vinyl chloride. As mentioned above, although the polymerization of a vinyl chloride was mainly explained, the distributed stabilizer of this invention is not necessarily limited to vinyl chlorides, and can be used for the suspension polymerizations of a vinyl system compound of arbitration, such as styrene, methacrylate, and vinyl acetate.

[0021]

[work --] for The PVA system resin of this invention has a carbonyl group in intramolecular, and contains 2 - trivalent a metaled salt or a metaled hydroxide. When each absorbance of 215nm according especially to the ultraviolet absorption spectrum of the 0.1-% of the weight water solution of this PVA system resin, 280nm, and 320nm is 0.4 or more preferably 0.18 or more, When the distributed stabilizer for suspension polymerizations of vinyl system compounds, such as a vinyl chloride, is presented, Excel in the dispersibility of the obtained vinyl chloride system polymer (resin) particle, and there is also little

coloring, and usefulness is very high as a distributed stabilizer for suspension polymerizations of a vinyl system compound, and it is also possible to use it as an assistant. The vinyl chloride by which the suspension polymerization was carried out using this distributed stabilizer can be used for the application of a film, a hose, a sheet, vinyl leather, a vinyl steel plate, water proof sail cloth, a coated fabric, an industrial manual bag, the roll for printing, a sole, foam, a doll, a cushion, etc.

[0022]

[Example] Hereafter, an example is given and this invention is explained in more detail. In addition, especially, it expresses weight criteria that it is with the "section" or "%", as long as there is no notice. Nitrogen-purge afterbaking of 0.0092% of the acetyl peroxide (APO) was prepared and carried out to the polymerization can to the example 1 <manufacture of distributed stabilizer> vinyl acetate 100 section, the acetaldehyde 1.2 section, the methanol 4.7 section, and vinyl acetate, the polymerization was started under the boiling point, and the polymerization was suspended when 91.8% of conversion was reached about 5.7 hours after reaction time. Subsequently, the vinyl acetate of a non-polymerization was removed, the obtained polymer was saponified with the conventional method by the sodium hydroxide, and the saponification slurry (methyl acetate/methanol = 8/2 (weight ratio) of solvents) of PVA system resin (a degree of polymerization 770, whenever [saponification] amount % of 0.16 mols of 71.7-mol % and carbonyl groups) of 12% of pitches was prepared.

[0023] Next, 10% methanol solution of magnesium acetate 4 hydrate was added at a rate of 350g to 1kg of PVA system resin as metallic compounds to the PVA system resin prepared above, and the PVA system resin which performed the swing end by the nutsche after 1-hour churning at 25 degrees C, and contained 177micro mol/g of magnesium acetate was obtained. Subsequently, nitrogen:air after making it dry in 110 degrees C under nitrogen for 2 hours within a heat treatment can = having slushed the gas of 1:1 (volume ratio) in the heat treatment can at the rate of 100l./hr, and maintaining at 10% of oxygen densities, heat treatment was performed at 145 degrees C for 3 hours, and the PVA system resin of this invention was obtained. The property of the obtained PVA system resin was as follows.

Polymerization degree; 730 (it measures based on JIS K 6726)

saponification whenever; -- 72.0 mol % magnesium acetate content; -- 177micromol/g (it computes from the amount of content magnesium)

The absorbance in the wavelength of 430nm of an absorbance;0.5200.2 % of the weight water solution in the wavelength of 320nm of an absorbance;0.6810.1 % of the weight water solution in the wavelength of 280nm of an absorbance;0.6000.1 % of the weight water solution in the wavelength of 215nm of a 0.1-% of the weight water solution; in order to check the solubility of 0.258 and the above-mentioned PVA system resin, the rate of un-dissolving was investigated in the following ways.

[0024] (Solubility) After putting 5.0g of PVA system resin, and 120g of ion exchange water into an Erlenmeyer flask, agitating under a room temperature for 30 minutes and repeating churning at 80 more degrees C for 1 hour, solution temperature is lowered to 20 degrees C, and suction filtration of the whole quantity is carried out through the filter paper for chemical analyses of weight known (ag). Furthermore, after it repeated the actuation which washes and carries out suction filtration of the Erlenmeyer flask by 50g of water 3 times and 3l. of ion exchange water performed suction filtration further, this filter paper was dried at 105 degrees C for 3 hours, weight (bg) was measured, the rate of the dissolution (%) was computed by the bottom type, O and the rate of the dissolution made less than 99.990 x or more for 99.990, and the rate of the dissolution investigated solubility.

Rate (%) of the dissolution = $100 - [(b-a)/5.0 \times 100]$

[0025] <Suspension polymerization of a vinyl chloride> In the autoclave made from stainless steel with an equipped with the stirrer capacity of 100l., under churning The water 150 30-degree C section, Lauroyl peroxide is taught at a rate of the 0.2 sections as the vinylchloride monomer 100 section, the distributed stabilizer (PVA system resin of this invention) 0.09 section obtained by the above, and a polymerization catalyst. It adjusted to the polymerization temperature of 57 degrees C, agitating by engine-speed 400rpm, the suspension polymerization was performed, and vinyl chloride resin (bulk density = 0.600cc/g by JIS K 6721, a residual monomer = 0.2 ppm) was obtained. The physical properties of the obtained vinyl chloride resin were investigated in the following ways. (Dispersibility)

In order to investigate the dispersibility at the time of the polymerization of a distributed stabilizer, the mean particle diameter (micrometer) of the obtained vinyl chloride resin (particle) was measured by the dry type sieve analysis method using the wire gauze of the Tyler mesh criteria. That is, particle diameter becomes the dispersant addition (A:0.09 section, B:0.07 section) dependency of particle diameter is small, and good [polymerization stability] small, so that the dispersibility of a distributed stabilizer is good.

[0026] (Particle size distribution) The content of the big and rough particle on 42 meshes of JIS standard sieves and the very fine particle under 250 meshes is displayed by weight %.

(Initial coloring nature) The vinyl-chloride-resin (particle) 100 obtained section, the DOP(dioctyl phthalate)35 section, the epoxidized-soybean-oil 1 section, and the barium-zinc system stabilizer 2 section were fabricated with the extruder on the sheet of 0.65mm thickness, after performing roll kneading for 10 minutes at 140 degrees C. Next, these eight sheets were piled up, heat press forming was carried out for 5 minutes at 180 degrees C in all, the press plate was produced, and the existence of coloring (or discoloration) of this press plate front face was observed by viewing.

(Fish eye) the extruder after performing roll kneading for the vinyl-chloride-resin (particle) 100 obtained section, the DOP(dioctyl phthalate)50 section, the dioctyl tin laurate 3 section, the zinc stearate 1 section, the stearyl alcohol 0.5 section, and the carbon black 0.1 section for 3 minutes at 155 degrees C - the sheet of 0.3mm thickness -- fabricating -- 100mmx -- the generating number of the fish eye per 100mm was measured, and the number made two or less pieces O, and made three or more pieces x. [0027] After having performed the polymerization so that it might result in predetermined conversion according to an example 1 in the charge of the acetaldehyde shown in two to example 9 table 1, a methanol, and acetyl peroxide (APO), obtaining the distributed stabilizer (PVA system resin) shown in tables 2 and 3 and investigating solubility like an example 1, the suspension polymerization of a vinyl chloride as well as an example 1 was performed, and dispersibility, coloring nature, and a fish eye were investigated similarly.

In example of comparison 1 example 1, except having not made metallic compounds (magnesium acetate 4 hydrate) contain, it carried out like the example 1, the distributed stabilizer (PVA system resin) of a publication was obtained to tables 2 and 3, and solubility, particle size distribution, dispersibility, coloring nature, and a fish eye were investigated similarly.

In example of comparison 2 example 1, except having replaced with magnesium acetate 4 hydrate as metallic compounds, and having used sodium acetate, it carried out like the example 1, the distributed stabilizer (PVA system resin) of a publication was obtained to tables 2 and 3, and solubility, particle size distribution, dispersibility, coloring nature, and a fish eye were investigated similarly. The solubility of an example and the example of a comparison, particle size distribution, dispersibility, coloring nature, and the measurement result of a fish eye are shown in a table 4.

[0028]

[A table 1]

Acetaldehyde MeOH APO Conversion (Section) (Section) (%) (%) Example 1 1.2 4.7 0.0092 91.8 ** 2 1.0 40 0.04 90.3 ** 3 1.0 50 0.05 91.4 ** 4 1.0 50 0.06 95.0 ** 5 1.260 0.07 95.0 ** 6 1.050 0.06 95.0 ** 7 1.0 50 0.06 95.0 ** 8 0.8 50 0.05 90.0 ** 9 0.6 30 0.03 20.0 ** MeOH expresses a methanol and APO expresses acetyl peroxide, respectively.

Each amount of the vinyl acetate used is the 100 sections.

[0029]

[A table 2]

Whenever [saponification] Degree of polymerization Carbonyl content Metallic compounds (Mol %) (Mol %) Class Content (mumol/g) example 1 71.1/72.0 770/730 0.16 Mg2 (OAc) 177 ** 2 72.0/73.0 800/768 0.134 Mg2 (OAc) 119 ** 3 72.0/72.5 730/704 0.16 Mg2 (OAc) 105 ** 4 71.5/71.8 700/690 0.17 Mg2 (OAc) 46 ** 5 71.5/72.8 650/616 0.19 Mg2 (OAc) 177 ** 6 71.5/73.0 700/690 0.17 calcium2 (OAc) 200 ** 7 71.5/73.2 700/690 0.17 P-calcium 300 ** 8 78.0/79.2 800/764 0.13 Mg2 (OAc) 100 ** 9 98.0/81.5 1600 / 15300.08 Mg2 (OAc) 65 Example of comparison 1 71.1/71.6 770/772 0.16 - - 2 71.1/72.5 770/800 0.16 NaOAc 177 Whenever [** saponification], and a degree of polymerization

express (value before heat treatment)/(value after heat treatment), and are KARUBO. A nil radical content expresses the value before heat treatment.

A code is as follows.

Mg₂ (OAc); magnesium acetate calcium₂ (OAc); calcium acetate P-calcium; calcium propionate NaOAc; sodium acetate [0030]

[A table 3]

The absorbance in each wavelength of a water solution 215nm 280nm 320nm 430nm Example 1 0.650 0.681 0.520 0.258 ** 2 0.632 0.660 0.540 0.250 ** 3 0.598 0.572 0.505 0.180 ** 4 0.525 0.510 0.510 0.230 ** 5 0.727 0.680 0.550 0.250 ** 6 0.580 0.660 0.495 0.250 ** 7 0.550 0.555 0.494 0.268 ** 80.700 0.660 0.500 0.280 ** 9 0.500 0.420 0.400 0.180 Example 1 of a comparison 0.300 0.230 0.324 0.410 ** 2 0.348 0.390 0.331 215nm of 0.600 **, 280nm and 320nm are 0.1-% of the weight water solutions, and is 430nm was measured in the water solution 0.2% of the weight, respectively.

[0031]

[A table 4]

Solubility Particle size distribution Dispersibility (micrometer) Coloring nature Fish eye (%) A B Example 1 O 0/0 115 119 Have no coloring. O ** 2 O 0/0 120 124 Have no coloring. O ** 3 O 0/0 123 128 Have no coloring. O ** 4 O 0/0 123 128 Have no coloring. O ** 5 O 0/0 118 122 Have no coloring. O ** 6 O 0/0 125 130 Have no coloring. O ** 7 O 0/0 125 135 With no coloring O ** 8 O 0/0 128 133 With no coloring O ** 9 O 0/0 130 135 Have no coloring. O Example 1 of a comparison O 0.2/0.1 135 Those with * coloring x ** 2 x 0.2/0 131 * Those with coloring x The block generated ** * and a uniform dispersed system was not acquired.

Particle size distribution express (content % of big and rough particle of 4.2 or more meshes)/(content [of the very fine particle under 250 mesh] %), and, for A and B, the addition of a distributed stabilizer is 0, respectively. The dispersibility assessment at the time of being the .09 section and the 0.07 sections is expressed.

[0032] In example 10 example 1, except having made the distributed stabilizer into the 0.1 sections and having made polymerization temperature into 66 degrees C, it carried out like the example 1, and mean particle diameter was able to obtain about 130 micrometers, and bulk specific gravity was able to obtain the vinyl chloride resin of 0.6400 cc/g.

In example of comparison 3 example 10, although the polymerization was similarly performed using the distributed stabilizer of the example 2 of a comparison, in order to have not stabilized a polymerization but to have obtained the vinyl chloride particle of this level mostly with the example 10, compared with the example 10, about 20% of distributed stabilizer needed to be increased.

[0033]

[Effect of the Invention] The PVA system resin of this invention has a carbonyl group in intramolecular, and contains 2 - trivalent a metaled salt or a metaled hydroxide. When each absorbance of 215nm according especially to the ultraviolet absorption spectrum of the 0.1-% of the weight water solution of this PVA system resin, 280nm, and 320nm is 0.4 or more preferably 0.18 or more, When the distributed stabilizer for suspension polymerizations of vinyl system compounds, such as a vinyl chloride, is presented, Excel in the dispersibility of the obtained vinyl chloride system polymer (resin) particle, and there is also little coloring, and usefulness is very high as a distributed stabilizer for suspension polymerizations of a vinyl system compound, and it is also possible to use it as an assistant. The vinyl chloride by which the suspension polymerization was carried out using this distributed stabilizer can be used for the application of a film, a hose, a sheet, vinyl leather, a vinyl steel plate, water proof sail cloth, a coated fabric, an industrial manual bag, the roll for printing, a sole, foam, a doll, a cushion, etc.

[Translation done.]